



Published in final edited form as:

*Polyhedron*. 2014 December 14; 84: 103–110. doi:10.1016/j.poly.2014.06.041.

## Carbon Dioxide Cleavage by a Ni<sub>2</sub> Complex Supported by a Binucleating Bis(N-Heterocyclic Carbene) Framework

Emily Y. Tsui and Theodor Agapie\*

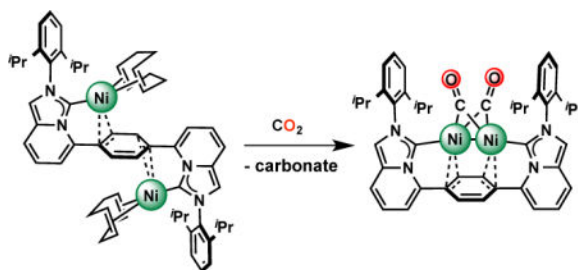
Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 E. California Blvd. MC 127-72 Pasadena, CA 91125

### Abstract

A binucleating bis(N-heterocyclic carbene) ligand was designed as a means to coordinate and proximally constrain two transition metal centers. Using an imidazopyridine-based NHC afforded a framework structurally related to previously reported *para*-terphenyl diphosphines. Bimetallic copper, cobalt, and nickel complexes supported by this framework were synthesized and structurally characterized. Strong interactions between the metal centers and the central arene were observed in all nickel complexes. Dinickel(0) complexes of this ligand framework were found to react with CO<sub>2</sub> to form a dicarbonyl-bridged dinickel(0) product, demonstrating facile CO<sub>2</sub> reduction.

### TOC image

First row transition metal complexes of a dinucleating bis(N-heterocyclic carbene) framework containing a arene moiety were synthesized and characterized structurally. Dinickel(0) complexes supported by this ligand react with CO<sub>2</sub> at room temperature to cleave a C=O bond and to form a dicarbonyl-bridged dinickel(0) complex.



## 1. Introduction

In recent years, multimetallic complexes have become attractive synthetic targets due to their potential uses in chemical transformations involving the transfer of multiple electrons through cooperative substrate binding and functionalization, particularly as several enzymatic active sites are known to contain multiple metal centers.<sup>1</sup> As such, there have been many efforts to design and synthesize new binucleating ligand frameworks.<sup>2</sup> Our group

agapie@caltech.edu.

Dedicated to Prof. John E. Bercaw on the occasion of his 70<sup>th</sup> birthday.

has used a *para*-terphenyl diphosphine ligand (**A**) to support a variety of binuclear Ni (Fig. 1, left), Pd, Fe, and Co complexes.<sup>3</sup> Labile metal-arene interactions between the metal centers and the central arene moiety have been observed in these compounds, with the proposed effect of stabilizing and electronically tuning these binuclear moieties.

Over the past two decades, N-heterocyclic carbene (NHC) ligands have gained prominence in organometallic chemistry and catalysis since they were first popularized by Arduengo and co-workers.<sup>5</sup> There have been many examples of polydentate NHC ligand frameworks; although these have primarily been chelating ligands that support a single metal center,<sup>6</sup> some support multimetallic complexes.<sup>7</sup> A new dinucleating NHC ligand framework (Fig. 1, right) containing an aryl linker was designed to incorporate both the hemilabile arene moiety of **A** and the different donor properties of the NHC donors compared to phosphines. In this work, we describe the synthesis of this ligand framework and of binuclear first row transition metal complexes, as well as initial reactivity studies.

## 2. Experimental

### 2.1 General Considerations

Unless stated otherwise, all synthetic manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere, or in a M. Braun glovebox under a nitrogen atmosphere. Reactions were carried out in oven-dried glassware cooled under vacuum. Anhydrous THF was purchased from Aldrich in 18 L Pure-Pac™ containers. Anhydrous benzene, hexanes, pentane, diethyl ether, and THF were purified by sparging with nitrogen for 15 minutes and then passing under nitrogen pressure through a column of activated A2 alumina (Zapp's). All non-dried solvents used were reagent grade or better. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. C<sub>6</sub>D<sub>6</sub> was dried over sodium/benzophenone ketyl, degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. Deuterated dichloromethane (CD<sub>2</sub>Cl<sub>2</sub>) was dried over calcium hydride, degassed by three freeze-pump-thaw cycles, and vacuum-transferred prior to use. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Varian 300, 400, or 500 MHz instruments, with shifts reported relative to the residual solvent peaks (7.16 and 128.06 ppm respectively for C<sub>6</sub>D<sub>6</sub>, 5.32 and 53.84 ppm respectively for CD<sub>2</sub>Cl<sub>2</sub>, and 7.27 and 77.16 ppm respectively for CDCl<sub>3</sub>). <sup>19</sup>F NMR spectra were referenced relative to the lock signal of the solvent. Elemental analyses were performed by Robertson Microlit, Ledge wood, NJ. High resolution mass spectrometry (HRMS) was performed at the California Institute of Technology Mass Spectrometry Facility. IR spectra were collected as thin films on a Bruker Alpha FT-IR spectrometer with a diamond ATR attachment.

Unless indicated otherwise, all reagents were used as received. Silver triflate was purchased from Alfa Aesar. Chloromethyl pivalate was purchased from Alfa Aesar and distilled from calcium hydride. Copper(I) chloride, nickel bis(cyclooctadiene), sodium *tert*-butoxide, and nickel(II) chloride dimethoxyethane adduct were purchased from Strem. Co[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>8</sup> 1,4-benzenediboronic acid<sup>9</sup> and 2-(2,6-diisopropylphenyl)imine-6-bromopyridine<sup>10</sup> were prepared according to literature procedures.

## 2.2 Synthesis of compounds

Preparation of 5-bromo-2-(2',6'-diisopropylphenyl)imidazo[1,5-*a*]pyridinium triflate. In the glovebox, silver trifluoromethanesulfonate (5.21 g, 20.27 mmol) was suspended in methylene chloride (15 mL) in a scintillation vial equipped with a stir bar. Chloromethyl pivalate (2.92 mL, 20.27 mmol) was added via syringe, and the mixture was stirred at room temperature in the dark for 45 min., changing to a dark red mixture. The mixture was filtered through Celite to remove silver chloride and washed with methylene chloride, then added to a solution of 2-(2,6-diisopropylphenyl)imine-6-bromopyridine (5.0 g, 14.48 mmol) in methylene chloride (5 mL). The dark red-brown solution was transferred to a reaction bomb equipped with a stir bar that was then sealed with a Teflon stopper. The reaction was stirred at 45 °C in the dark for 16 h, then cooled to room temperature. Ethanol (10 mL) was added to quench the reaction and the mixture was concentrated *in vacuo* to yield a viscous brown oil that crystallizes upon standing. The solid was washed with diethyl ether and then recrystallized from diethyl ether/methylene chloride to yield the product as a white solid (5.27 g, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 9.24 (d, *J* = 1.8 Hz, 1 H, NC(H)N), 8.48 (d, *J* = 1.8 Hz, 1 H), 8.33 (d, *J* = 9.0 Hz, 1 H, *o*-Br), 7.63 (t, *J* = 8.0 Hz, 1 H, *m*-Br), 7.57 (d, *J* = 7.2 Hz, 1 H), 7.40–7.33 (m, 3 H), 2.14 (sept, *J* = 6.6 Hz, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (d, *J* = 6.6 Hz, 6 H, CH<sub>3</sub>), 1.21 (d, *J* = 6.6 Hz, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 145.2, 132.7, 132.6, 130.4, 126.6, 125.7, 125.0, 124.0, 119.7, 119.5, 112.0, 28.9, 24.6, 24.4 ppm. HRMS (FAB+, *m/z*) for C<sub>18</sub>H<sub>22</sub>BrN<sub>2</sub>: 357.0966. Found: 357.0951.

**Preparation of DIPr•2HCl**—A reaction bomb equipped with a stir bar was charged with 5-bromo-*N*-(2,6-diisopropylphenyl)imidazo[1,5-*a*]pyridinium triflate (12.915 g, 25.45 mmol), 1,4-benzenediboronic acid (2.11 g, 12.73 mmol), potassium carbonate (10.55 g, 76.36 mmol), toluene (200 mL), ethanol (40 mL), and water (40 mL). The mixture was degassed via three freeze-pump-thaw cycles, then Pd(PPh<sub>3</sub>)<sub>4</sub> (0.735 g, 0.636 mmol) was added under N<sub>2</sub>. The flask was sealed with a Teflon stopper, then heated to 100 °C for 22 h. The mixture was cooled to room temperature, then the organics were extracted with ethyl acetate and dichloromethane, dried over magnesium sulfate, filtered, then concentrated under reduced pressure. The resulting brown solid was recrystallized from diethyl ether/dichloromethane to yield an off-white solid. The solid was dissolved in dichloromethane (50 mL), then tetrabutylammonium chloride (2.75 g) was added. The mixture was stirred for 2 h, then concentrated under reduced pressure. The residue was taken up in diethyl ether/THF, and the solid was collected, washed with THF, then recrystallized from diethyl ether/chloroform to yield the product as a white solid (2.43 g, 27%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 12.19 (s, 2 H, NC(H)N), 7.99 (d, *J* = 9.3 Hz, 2 H, Ar-H), 7.87 (s, 4 H, central arene), 7.85 (d, *J* = 1.5 Hz, 2 H, Ar-H), 7.56 (t, *J* = 7.8 Hz, 2 H, Ar-H), 7.49 (dd, *J* = 9.3, 6.9 Hz, 2 H, Ar-H), 7.30 (d, *J* = 7.8 Hz, 4 H, Ar-H), 7.25 (d, *J* = 6.9 Hz, 2 H, Ar-H), 2.06 (sept, *J* = 6.9 Hz, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (d, *J* = 6.9 Hz, 12 H, CH<sub>3</sub>), 1.11 (d, *J* = 6.9 Hz, 12 H, CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.463 MHz): δ 141.7, 135.8, 134.4, 133.6, 131.80, 131.75, 131.0, 129.8, 129.1, 126.0, 118.8, 118.7, 115.7, 21.3, 17.8 ppm. HRMS (FAB+) for C<sub>44</sub>H<sub>48</sub>N<sub>4</sub>Cl: 667.3567. Found: 667.3560.

**Preparation of DIPr[CuCl]<sub>2</sub> (2)**—In the glovebox, a scintillation vial equipped with a stir bar was charged with DIPr•2HCl (0.040 g, 0.057 mmol), sodium *tert*-butoxide (0.011 g, 0.11

mmol, 2 equiv), and copper(I) chloride (0.011 g, 0.11 mmol, 2 equiv). THF (5 mL) was added, and the yellow mixture was stirred at room temperature for 2 h. The mixture was filtered through Celite to remove an insoluble yellow precipitate, and the yellow filtrate was concentrated *in vacuo*. The mixture was washed with benzene, then extracted with THF and concentrated again under reduced pressure to yield a yellow solid. This solid was washed with acetonitrile to yield the product as a yellow solid (0.011 g, 23%). X-ray quality single crystals were grown by vapor diffusion of diethyl ether into a dichloromethane solution of **2**.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz):  $\delta$  7.79 (s, 4 H, central arene), 7.52 (d,  $J$  = 7.6 Hz, 2 H, Ar-H), 7.48 (d,  $J$  = 9.6 Hz, 2 H, Ar-H), 7.38 (s, 2 H, benzylic H), 7.30 (d,  $J$  = 8.0 Hz, 4 H, Ar-H), 7.13–7.09 (m, 4 H, Ar-H), 2.26 (sept,  $J$  = 6.8 Hz, 4 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.20 (d,  $J$  = 6.8 Hz, 12 H,  $\text{CH}_3$ ), 1.14 (d,  $J$  = 6.8 Hz, 12 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 101 MHz):  $\delta$  145.8, 139.4, 136.3, 136.2, 132.1, 130.1, 130.7, 124.4, 124.3, 117.3, 116.6, 114.3, 28.7, 24.7, 24.4 ppm. Anal. Calcd. For  $\text{C}_{44}\text{H}_{46}\text{Cl}_2\text{Cu}_2\text{N}_4$ : C, 63.76; H, 5.59; N, 6.76 %. Found: C, 63.51; H, 5.31; N, 6.51 %.

**Preparation of  $\text{DIPr}[\text{Co}(\text{Cl})\text{N}(\text{SiMe}_3)_2]_2$  (**3**)**—In the glovebox, a scintillation vial equipped with a stir bar was charged with  $\text{DIPr}\cdot 2\text{HCl}$  (0.046 g, 0.065 mmol) and  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$  (0.050 g, 0.13 mmol, 2 equiv). Benzene (6 mL) was added, and the green mixture was stirred for 12 h, then filtered through Celite and concentrated under reduced pressure. The yellow-brown residue was washed with pentane, then extracted with diethyl ether and concentrated *in vacuo*. A benzene solution was allowed to stand at room temperature, slowly forming the product as yellow crystals (0.008 g, 11%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  89.0 ( $\nu_{1/2}$  = 65 Hz), 64.6 ( $\nu_{1/2}$  = 90 Hz), 36.1 ( $\nu_{1/2}$  = 53 Hz), 10.1 ( $\nu_{1/2}$  = 104 Hz), 3.3 ( $\nu_{1/2}$  = 371 Hz),  $-2.3$  ( $\nu_{1/2}$  = 442 Hz),  $-7.2$  ( $\nu_{1/2}$  = 26 Hz),  $-15.2$  ( $\nu_{1/2}$  = 115 Hz),  $-51.1$  ( $\nu_{1/2}$  = 42 Hz),  $-54.8$  ( $\nu_{1/2}$  = 324 Hz),  $-70.0$  ( $\nu_{1/2}$  = 942 Hz) ppm.

**Preparation of  $\text{DIPr}[\text{Ni}(\mu\text{-Cl})]_2$  (**4**)**—In the glovebox, a round-bottom flask equipped with a stir bar was charged with  $\text{DIPr}\cdot 2\text{HCl}$  (1.18 g, 1.68 mmol), sodium *tert*-butoxide (0.327 g, 3.4 mmol), nickel bis(cyclooctadiene) (0.459 g, 1.67 mmol), and nickel dichloride dimethoxyethane adduct (0.367 g, 1.67 mmol). THF (100 mL) was added, and the brown mixture was stirred at room temperature for 12 h. The dark brown mixture was filtered through Celite, washing with THF (50 mL), and the filtrate was concentrated *in vacuo*. The brown residue was taken up in benzene (60 mL), filtered through Celite, then concentrated *in vacuo*. The resulting brown solid was washed with pentane (30 mL), and dried under vacuum to yield the product as a brown solid (0.300 g, 22%). X-ray quality single crystals were grown by vapor diffusion of pentane into a diethyl ether solution of **4** at room temperature.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz):  $\delta$  14.34 (s, 4 H, central arene), 8.49 (s, 2 H, benzylic H), 7.59 (d,  $J$  = 7.0 Hz, 4 H, Ar-H), 7.53 (t,  $J$  = 7.0 Hz, 2 H, Ar-H), 7.19 (d,  $J$  = 9.5 Hz, 2 H, Ar-H), 6.94 (d,  $J$  = 6.5 Hz, 2 H, Ar-H), 5.86 (dd,  $J$  = 6.5, 9.5 Hz, 2 H, Ar-H), 2.86 (sept,  $J$  = 6.5 Hz, 4 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.64 (d,  $J$  = 6.5 Hz, 12 H,  $\text{CH}_3$ ), 1.12 (d,  $J$  = 6.5 Hz, 12 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 126 MHz):  $\delta$  157.4, 150.7, 150.0, 149.4, 148.7, 147.9, 147.4, 147.2, 131.1, 125.0, 122.3, 117.4, 109.3, 33.18, 27.8, 25.6 ppm.

**Preparation of  $\text{DIPr}[\text{Ni}(\text{COD})]_2$  (**5**)**—In the glovebox, an oven-dried round-bottom flask equipped with a stir bar was charged with  $\text{DIPr}\cdot 2\text{HCl}$  (0.200 g, 0.284 mmol), sodium *tert*-butoxide (0.055 g, 0.572 mmol, 2 equiv), and  $\text{Ni}(\text{COD})_2$  (0.150 g, 0.546 mmol, 1.9 equiv). Benzene (40 mL) was added, and the mixture was stirred for 90 min. at room temperature, turning from yellow to green to dark brown. The mixture was then filtered through Celite, then concentrated *in vacuo* to yield a dark brown solid. This residue was washed with hexanes (50 mL) and diethyl ether (10 mL), then dried under vacuum to yield the product as a dark brown solid (0.150 g, 55%). Due to the equilibrium between **5** and **6** in benzene solution, NMR spectra were collected after the addition of 2 equivalents of excess 1,5-cyclooctadiene.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  7.26 (t,  $J$  = 7.6 Hz, 2 H, Ar-H), 7.13 (d,  $J$  = 7.6 Hz, 4 H, Ar-H), 6.79 (s, 2 H, Ar-H), 6.65 (d,  $J$  = 8.8 Hz, 2 H, Ar-H), 6.45 (d,  $J$  = 6.4, 10.4 Hz, 2 H, Ar-H), 6.34 (d,  $J$  = 6.8 Hz, 2 H, Ar-H), 6.25 (bs, 4 H, central arene), 4.2 (bs, 8 H,  $\text{Ni}(\text{COD})$  vinyl H), 2.82 (sept,  $J$  = 6.8 Hz, 4 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.9 (bs, 12 H,  $\text{Ni}(\text{COD})$  methylene H), 1.28 (d,  $J$  = 6.8 Hz, 12 H,  $\text{CH}_3$ ), 0.96 (d,  $J$  = 6.8 Hz, 12 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 100.5 MHz):  $\delta$  194.33, 148.09, 146.27, 138.10, 130.78, 129.74, 128.83, 125.14, 123.75, 112.49, 111.88, 106.14, 81.04, 30.70, 28.72, 26.54, 22.36 ppm.

**Preparation of  $\text{DIPr}[\text{Ni}(\text{C}_6\text{H}_6)]_2$  (**6**)**—Procedure A: In the glovebox, a scintillation vial equipped with a stir bar was charged with a solution of **4** (0.272 g, 0.333 mmol) in THF (10 mL). A 1 M THF solution of  $\text{LiBEt}_3\text{H}$  (0.67 mL, 0.666 mmol) was added via syringe. The mixture was stirred at room temperature for 10 min. and the mixture was concentrated *in vacuo*. The brown residue was taken up in benzene, filtered through Celite, then concentrated *in vacuo*. The resulting solid was washed with hexanes and diethyl ether to yield the product as a brown solid (0.074 g, 25%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz):  $\delta$  7.15 (2 H, overlapped with solvent residual peak, identified by gCOSY), 7.07 (d,  $J$  = 7.5 Hz, 2 H, Ar-H), 6.99 (d,  $J$  = 7.5 Hz, 2 H, Ar-H), 6.89 (d,  $J$  = 6.5 Hz, 2 H, Ar-H), 6.85 (d,  $J$  = 9.0 Hz, 2 H, Ar-H), 6.80 (s, 2 H, Ar-H), 6.56 (t,  $J$  = 8.0 Hz, 2 H, Ar-H), 5.56 (s, 2 H, central arene H), 3.53 (s, 2 H, central arene H), 2.63 (sept,  $J$  = 7.0 Hz, 2 H,  $\text{CH}(\text{CH}_3)_2$ ), 2.17 (sept,  $J$  = 7.0 Hz, 2 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.15 (d,  $J$  = 7.0 Hz, 6 H,  $\text{CH}_3$ ), 1.01 (d,  $J$  = 7.0 Hz, 6 H,  $\text{CH}_3$ ), 0.93 (d,  $J$  = 7.0 Hz, 6 H,  $\text{CH}_3$ ), 0.91 (d,  $J$  = 7.0 Hz, 6 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 126 MHz):  $\delta$  129.4, 147.6, 147.1, 145.4, 137.3, 130.7, 129.7, 125.3, 123.8, 123.5, 112.8, 112.4, 106.8, 105.7, 97.3, 42.4, 28.6, 28.5, 26.7, 24.7, 24.2, 22.6 ppm. Compound **6** is unstable at room temperature and decomposes in solution and in the solid-state over several hours.

Procedure B: In the glovebox, a Schlenk flask equipped with a stir bar was charged with a benzene solution of **5**. The solution was degassed with three freeze-pump-thaw cycles, then placed under an atmosphere of dihydrogen. The reaction mixture was stirred for 30 min. at room temperature, then dried *in vacuo*. The resulting brown solid was washed with pentane to yield the product as a brown solid (0.023 g, 82%).

**Preparation of  $\text{DIPr}[\text{Ni}(\mu_2\text{-CO})]_2$  (**7**)**—Procedure A: In the glovebox, a J. Young NMR tube was charged with a solution of **6** (0.017 g, 0.019 mmol) in  $\text{C}_6\text{D}_6$  (0.7 mL). The solution was degassed via three freeze-pump-thaw cycles, then placed under an atmosphere of  $\text{CO}_2$ . The reaction was allowed to proceed at room temperature, and monitored by  $^1\text{H}$  NMR

spectroscopy. Compound **7** was identified as the major species in the mixture by  $^1\text{H}$  NMR spectroscopy after 20 h.

Procedure B: In the glovebox, a scintillation vial equipped with a stir bar was charged with **5** (0.021 g, 0.022 mmol) and paraformaldehyde (0.015 g, 0.044 mmol, 2 equiv). THF (5 mL) was added, and the brown mixture was stirred at room temperature for 1 h, turning dark purple. The mixture was concentrated *in vacuo*, then crystallized from diethyl ether/pentane to yield the product as a brown-purple solid (0.008 g, 47%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz):  $\delta$  7.10 (t,  $J$  = 7.0 Hz, 2 H, Ar-H), 7.03 (d,  $J$  = 7.0 Hz, 4 H, Ar-H), 6.81 (s, 2 H, Ar-H), 6.74 (dd,  $J$  = 2.0, 7.8 Hz, 2 H, Ar-H), 6.38 (m, 4 H, Ar-H), 6.24 (bs, 4 H, central arene), 2.64 (sept,  $J$  = 7.0 Hz, 4 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.27 (d,  $J$  = 7.0 Hz, 12 H,  $\text{CH}_3$ ), 0.99 (d,  $J$  = 7.0 Hz, 12 H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 126 MHz):  $\delta$  184.9, 145.5, 142.9, 137.4, 129.8, 127.2, 124.1, 123.8, 115.0, 114.3, 112.5, 109.9, 98.3 (bs, located at 50 °C), 28.6, 24.8, 23.8 ppm. The  $^{13}\text{C}$  signal corresponding to the carbonyl ligands could not be located, presumably due to fluxional exchange processes. FT-IR (ATR film,  $\text{C}_6\text{D}_6$ ): 1825  $\text{cm}^{-1}$  (CO).

### 3. Results and Discussion

#### 3.1 Synthesis of ligand framework

The bis(carbene) precursor, abbreviated DIPr•2HCl, was prepared in three steps from commercially available starting materials based upon a previously published route.<sup>11</sup> Condensation of 2-bromo-6-pyridinecarboxaldehyde with 2,6-diisopropylaniline yielded the corresponding imine (Scheme 1). Cyclization by treatment with silver triflate and chloromethyl pivalate formed the bromo-substituted imidazo[1,5-a]pyridinium salt. Suzuki coupling of this imidazo[1,5-a]pyridinium triflate with 1,4-benzenediboronic acid, followed by anion substitution using tetrabutylammonium chloride, yielded the ligand precursor DIPr•2HCl.

#### 3.2 Metallation with copper(I) and cobalt(II)

A small number of monometallic complexes supported by mono-NHC versions of DIPr are known, with Cu, Pd, Ir, Rh, and Au.<sup>11–12</sup> With the ligand precursor DIPr•2HCl in hand, bimetallic complexes of the bis(carbene) framework were targeted. Attempts to deprotonate DIPr•2HCl using bases such as sodium *tert*-butoxide, sodium hydride, or sodium bis(trimethylsilyl)amide to yield the free bis(carbene) resulted in intractable mixtures of insoluble products, possibly due to decomposition of the free carbene. Fortunately, one-pot metallation reactions of DIPr•2HCl proved to be more successful. Treatment of DIPr•2HCl with two equivalents of sodium *tert*-butoxide and two equivalents of copper(I) chloride in THF formed the corresponding dicopper(I) dichloride compound DIPr[CuCl]<sub>2</sub> (**2**, Scheme 2). X-ray quality crystals were grown from vapor diffusion of diethyl ether into a dichloromethane solution of **2**. A X-ray diffraction (XRD) study of these crystals (Fig. 2 left) showed that the two copper(I) centers are oriented on opposite faces of the central arene, and are coordinated in a linear geometry (C–Cu–Cl angle of 175.3(2)°). Compound **2** is structurally related to a monomeric and less sterically hindered version,<sup>12d</sup> whose solid-state structure displays a Cu–Cl distance of 2.102 Å and a Cu–C distance of 1.875 Å (average of two molecules in the asymmetric unit). In comparison, compound **2** has a Cu–Cl



distance of 2.210(5) Å and a Cu–C distance of 1.886(2) Å. Although the imidazopyridine-based NHC has higher donor ability,<sup>12b</sup> the above structures are similar to that of a copper complex supported by an imidazole-based NHC (IPrCuCl),<sup>13</sup> with Cu–Cl distance of 2.106(2) Å and a C–Cu distance of 1.881(7) Å. No interactions with the central arene are observed in the XRD structure (shortest Cu–C(arene) distance 3.06 Å); this is also borne out in the <sup>1</sup>H NMR spectrum, in which the signal corresponding to the central arene protons is located at 7.79 ppm.

Rather than use an exogenous base, DIPr•2HCl can also be metallated via aminolysis of metal amide compounds. The addition of two equivalents of Co[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> to DIPr•2HCl in benzene results, after two days at room temperature, in yellow crystals of the dicobalt(II) compound DIPr[Co(Cl)N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**3**, Fig. 2 right). As with **2**, the two metal centers are oriented on opposite faces of the central arene and no metal–arene interactions are observed (shortest Co–C(arene) distance 2.95 Å). The coordination sphere of each cobalt(II) center is completed by a single chloride and bis(trimethylsilyl)amide ligand. A related monocobalt complex with Cl<sup>−</sup>, N(SiMe<sub>3</sub>)<sub>2</sub><sup>−</sup>, and imidazole-based NHC ligands has previously been isolated and structurally characterized.<sup>14</sup> The <sup>1</sup>H NMR spectrum of a C<sub>6</sub>D<sub>6</sub> solution of **3** displays broad peaks between −70 and 90 ppm, consistent with a paramagnetic compound.

### 3.3 Synthesis of dinickel complexes

Although compounds **2** and **3** are bimetallic, the metal centers are located on opposite faces of the central arene, potentially limiting access to cooperative reactivity. To test the ability of ligand DIPr to support metals in close proximity with potential for bimetallic reactivity species displaying metal–metal interactions were targeted. Both NHC ligands and diphosphine **A** have been shown to support dinickel(I) dichloride complexes containing a Ni<sup>I</sup>–Ni<sup>I</sup> bond. These complexes were prepared by the comproportionation of NiCl<sub>2</sub>(dme) (dme = 1,2-dimethoxyethane) and Ni(COD)<sub>2</sub> (COD = 1,5-cyclooctadiene) (Fig. 1, left and center).<sup>3a, 4</sup> Treatment of a THF suspension of DIPr•2HCl with sodium *tert*-butoxide (2 equiv) and equimolar amounts of Ni(COD)<sub>2</sub> and NiCl<sub>2</sub>(dme) resulted in the formation of comproportionation product DIPr[Ni(μ-Cl)]<sub>2</sub> (**4**) as a dark brown solid (Scheme 3). As with both the NHC-supported and diphosphine-supported complexes, the <sup>1</sup>H NMR spectrum of **4** is diamagnetic, consistent with a Ni<sup>I</sup>–Ni<sup>I</sup> interaction. The signal corresponding to the central arene protons is a downshifted singlet at 14.24 ppm. In comparison, the central arene <sup>1</sup>H NMR signal of the corresponding diphosphine-supported dinickel(I) dichloride complex **1** is shifted upfield from that of free ligand,<sup>3a</sup> indicating differences in the nickel–arene interactions. The observation of a singlet for the central arene and of only one methine peak for the isopropyl moieties, suggests that the dinickel(I) unit is involved in a fluxional process that exchanges positions over the central arene fast on the NMR timescale at room temperature.

Single crystals of **4** were grown by vapor diffusion of pentane into a diethyl ether solution of the complex. A XRD study shows that the two nickel(I) centers are located on the same face of the arene ring, with the two chlorides bridging the metal centers, and a Ni–Ni distance of 2.3936(3) Å (Fig. 3), shorter than previously reported Ni<sub>2</sub>(μ-Cl)<sub>2</sub> moieties supported by imidazole-NHC (Ni–Ni ~ 2.51 Å).<sup>4</sup> The shorter Ni–Ni distance in **4** may be a consequence

of the geometric constraints of the ligand framework that distorts at the aryl-aryl linkages due to the cofacial bimetallic moiety. There are strong interactions between the nickel centers and the central arene moiety, with short C–Ni distances (2.05–2.17 Å). Additionally, the C–C bond distances of the central arene show significant bond localization (Fig. 3 inset). The solid-state structure of compound **1** shows similar nickel-arene interactions (Ni–C distances 2.05–2.10 Å) and central arene bond localization distances. Due to the longer Ni–P distances (2.17–2.18 Å) compared to the Ni–C(carbene) distances (1.91 Å), the terphenyl backbone of the diphosphine ligand is more distorted to accommodate the dinickel moiety, with the outer aryl rings of the diphosphine bent 15–17° out of the plane vs. 9–10° for **4**. Compound **4** displays a torsion angle of 62.72–68.75°, while the pendant aryl groups of **1** are oriented closer to perpendicular to the central arene, with torsion angles of 74.4 and 78.8°. As a result, the nickel(I) centers of **4** are located further toward the C–H bonds compared to **1**, potentially causing the differences in the <sup>1</sup>H NMR spectra. The Ni–Ni distance is longer in **4** (2.3936(3) Å) compared to **1** (2.3658(2) Å), possibly a consequence of the differences in the ligand distortions, but also of the different electronic character of the ligands.<sup>12b</sup>

More reduced dinickel(0) compounds were also targeted, as a previous example of a NHC-supported dinickel(0) compound was demonstrated to be capable of CO<sub>2</sub> deoxygenation, presumably by the formation of an equivalent of a nickel carbonate species.<sup>15</sup> A benzene suspension of DIPr•2HCl was treated with sodium *tert*-butoxide and Ni(COD)<sub>2</sub> to form a dark brown compound **5** (Scheme 3). The <sup>1</sup>H NMR spectrum of a C<sub>6</sub>D<sub>6</sub> solution of **5** displays two broad signals at 4.2 and 1.9 ppm corresponding to the protons of the coordinated 1,5-cyclooctadiene ligands. Additionally, the signal corresponding to the central arene protons is shifted upfield, to 6.25 ppm, consistent with interactions between the nickel(0) centers and the central arene. A XRD study of single crystals of **5** grown from THF/hexanes at –35 °C (Fig. 4) confirmed the structure to be a dinickel(0) complex in which the metal centers are located on opposite faces of the central arene, each displaying an η<sup>2</sup>-interaction with the vicinal diene of the central arene moiety (Ni–C distances 2.13–2.15 Å).

In benzene solution, compound **5** was observed to be in equilibrium with a second DIPr ligand-containing complex (**6**), along with free COD. Addition of excess COD resulted in complete conversion to **5**, however. Compound **6** is proposed to be the benzene adduct of the dinickel(0) complex. Addition of excess dihydrogen to a benzene solution of **5** facilitates hydrogenation of COD and formation of clean **6** (<sup>1</sup>H NMR spectroscopy). Compound **6** can also be independently prepared by reduction of the dinickel(I) compound **4** with two equivalents of LiBEt<sub>3</sub>H or two equivalents of sodium naphthalenide in THF, followed by benzene. Unfortunately, compound **6** is unstable at room temperature in solution and in the solid-state, decomposing within several hours. As such, it has been challenging to grow X-ray quality single crystals of **6**, and structural confirmation of its assignment via XRD has not been achieved yet. The <sup>1</sup>H NMR spectrum of a C<sub>6</sub>D<sub>6</sub> solution of **6** displays two singlets integrating to 2 protons corresponding to the central arene at 5.56 and 3.53 ppm, both shifted far upfield relative to **5**, consistent with greater backbonding into the central arene ligand due to weaker backbonding into the coordinated benzene ligands compared to COD. The



observation of two central arene signals, as well as two isopropyl methine signals, indicates that the fluxional motion of the nickel centers is slower than that of **4** and **5**, again consistent with stronger metal-arene interactions. In comparison, reduction of phosphine-based system **1** or metallation of **A** with nickel(0) sources has typically yielded only a mononickel(0) complex rather than dinickel complexes, except in cases in which the compounds are stabilized via bridging carbonyl ligands.<sup>3d, 16</sup> These differences may be a consequence of the structural parameters of ligands **A** and DIPr. The shorter M–C compared to M–P bond distances and the steric profile of the *para*-terphenyl linker are expected to disfavor mononickel(0) complexes with DIPr vs **A**.

### 3.4 CO<sub>2</sub> reactivity studies

Nickel complexes have long been examined for carbon dioxide reduction activity due to the proposed role of the nickel center in carbon monoxide dehydrogenase.<sup>17</sup> The first known example of a nickel carbon dioxide complex, (Cy<sub>3</sub>P)<sub>2</sub>Ni(CO<sub>2</sub>) was prepared by Aresta and coworkers in 1975.<sup>18</sup> In this example, the CO<sub>2</sub> complex was found to yield small amounts of carbonyl and carbonate products upon heating via the metal-mediated disproportionation of CO<sub>2</sub>. Other examples of tri- and diphosphine supported nickel(0) complexes have been demonstrated to cleave CO<sub>2</sub> via the formation of nickel carbonyl and carbonate complexes, or via the oxidation of the phosphine ligands to form phosphine oxides.<sup>19</sup> A recent report by Caulton and co-workers described the cleavage of the C–O bond of CO<sub>2</sub> by a PNP pincer-supported nickel(I) complex to transpose an oxygen center from CO<sub>2</sub> with the amide nitrogen of the ligand framework.<sup>20</sup> Multinickel complexes have also been studied for the reduction of carbon dioxide. Sadighi and co-workers reported a dinickel(0) compound that reacts with CO<sub>2</sub> to form a carbonyl-bridged dinickel complex with proposed concomitant loss of an unobserved nickel carbonate species.<sup>15</sup> A recent example of dinickel(I) complexes supported by  $\beta$ -diketiminate ligands also demonstrated the formation of carbonyl, carbonate, and oxalate nickel complexes.<sup>21</sup> Dinickel and trinickel complexes have also been reported as effective electrocatalysts in the reduction of CO<sub>2</sub> to CO.<sup>22</sup>

Upon treatment of benzene solutions of **5** or **6** with excess CO<sub>2</sub>, complete consumption of starting material was observed by <sup>1</sup>H NMR spectroscopy within minutes to form one major species that has eluded isolation thus far. Over 7 hours at room temperature, this species converts to a mixture of products, with one major species (**7**) observed by <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR spectrum of **7** displays one signal for the isopropyl methine protons and a broad singlet at 6.2 ppm corresponding to the central arene ring, indicating nickel-arene interactions, albeit weaker than those observed in **6**. An IR spectrum of **7** shows a strong band at 1825 cm<sup>-1</sup>, consistent with the stretching vibration of a bridging CO moiety (Scheme 4).<sup>23</sup> When <sup>13</sup>CO<sub>2</sub> was added to **5**, a signal at 171 ppm was initially observed in the <sup>13</sup>C NMR spectrum (see supporting information), possibly indicating a carbon dioxide complex of nickel, while the final product mixture showed two sharp signals at 161 ppm, consistent with nickel carbonate complexes.<sup>24</sup> The <sup>13</sup>C signal corresponding to the bridging carbonyl ligands of **7** could not be observed by <sup>13</sup>C NMR spectroscopy even at elevated temperatures, possibly due to fluxional exchange processes of the dinickel unit about the central arene ring. Compound **7** was prepared independently from the reaction of **5** with paraformaldehyde.

A XRD study of crystals grown from vapor diffusion of pentane into a diethyl ether solution of **7** reveals the structure to be a dinickel(0) complex in which the two nickel centers are located on the same face of the central arene and are bridged by two  $\mu_2$ -CO ligands (Figure 5). Notably, the co-facial arrangement of metals supported by DIPr occurs in connection with small ligands that show a propensity to bridge ( $\text{Cl}^-$  or CO). The nickel centers also interact with the vicinal diene of the central arene in a similar manner as **4**, with bond localization of the central arene C–C bonds (Figure 5, inset). However, the dinickel moiety is located further from the *ipso*-carbons of the central arene than that of **4**, with torsion angles of 50.38–51.28° between the pendant and central aryl groups. The structure of compound **7** also displays an unusually short Ni–Ni distance (2.248(1) Å). In comparison, the Ni–Ni distance of compound **4** is 2.3936(3) Å and the median Ni–Ni distance of carbonyl-bridged species from a CSD search of dinickel complexes is 2.387 Å. This shorter vector compared to other carbonyl-bridged nickel species may be due to the constraints of the dinucleating ligand framework. The conversion of **5** to **7** indicates that the metal-arene interactions are hemilabile and allow for transfacial to cofacial isomerization. The isolation of **7** demonstrates that  $\text{CO}_2$  cleavage can occur at a dinickel complex supported by a binucleating NHC-based ligand to generate metal-CO species. Addressing the fate of the oxygen atom in an atom economical manner remains a challenge.

## 4. Conclusions

A novel bis(N-heterocyclic carbene) framework containing a central arene donor was prepared and employed to support dinuclear complexes of first row transition metals. Dicopper(I), dicobalt(II), and dinickel complexes of varying oxidation state were synthesized and structurally characterized. While the copper and cobalt complexes display metals on opposite sides of the central arene, the dinickel(I) complex is cofacial with a strong Ni–Ni interaction. This compound was utilized as a precursor to dinickel(0) species that reacted with  $\text{CO}_2$  to form a dicarbonyl-bridged dinickel(0) product. Although further elaboration of this chemistry will require a suitable acceptor for the oxygen atom, the current reactivity demonstrates that dinickel complexes supported by a binucleating NHC ligand can promote facile  $\text{CO}_2$  reduction.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

This work was supported by the California Institute of Technology, NSF CAREER Grant CHE-1151918, and a Sandia Campus Executive Fellowship (to E. Y. T.). We thank L. M. Henling for assistance with crystallography. The Bruker KAPPA APEXII X-ray diffractometer was purchased via an NSF Chemistry Research Instrumentation award to Caltech (CHE-0639094). The 400 MHz NMR spectrometer was purchased via NIH Award RR027690.

## Appendix A. Supplementary data

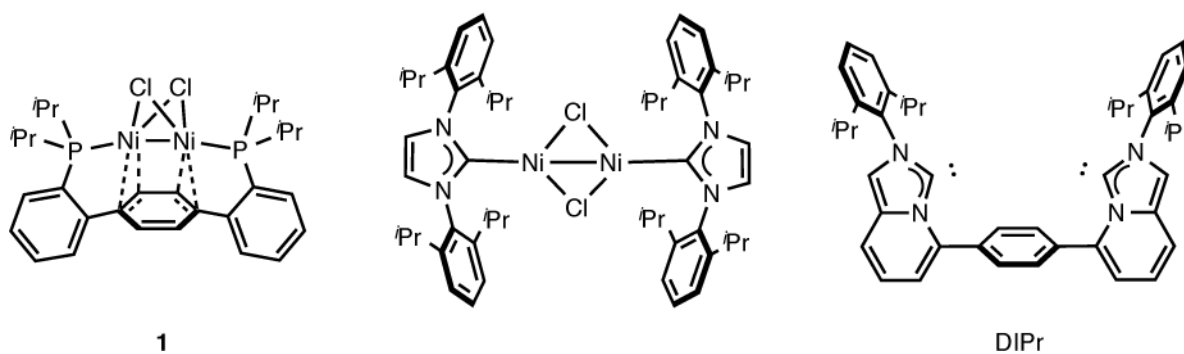
CCDC 999595-999599 contain the supplementary data for compounds **2**, **3**, **4**, **5**, and **7**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/>

[retrieving.html](#), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

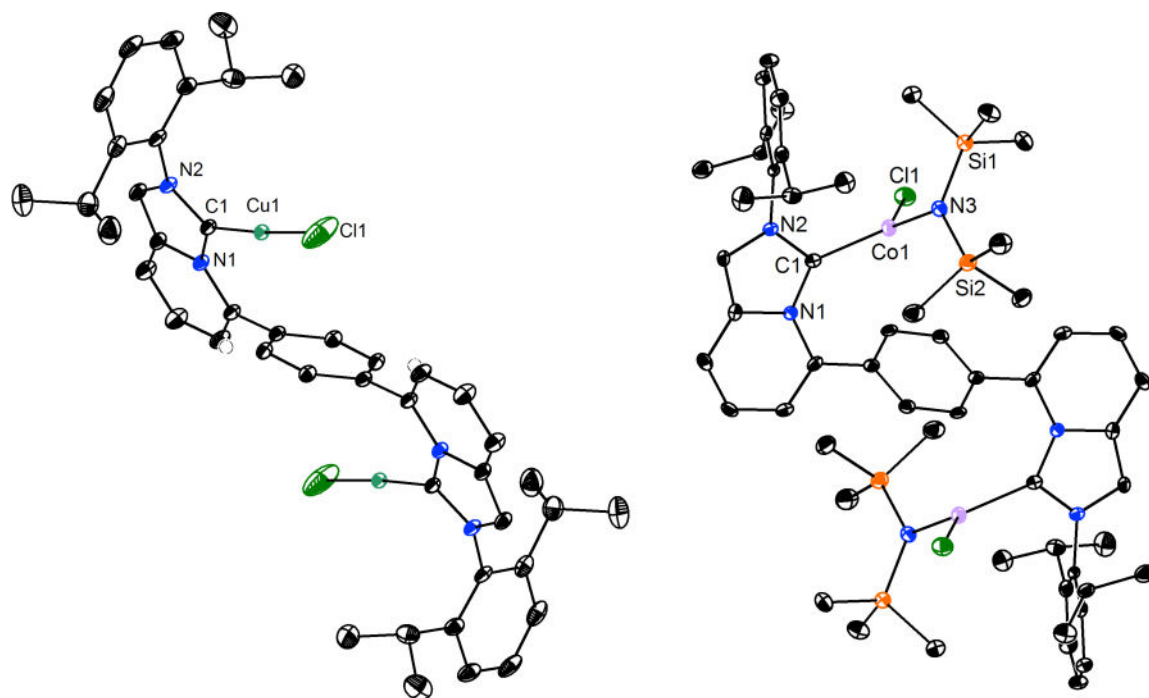
## References

1. Holm RH, Kennepohl P, Solomon EI. *Chem Rev.* 1996; 96:2239–2314. [PubMed: 11848828]
2. Gavrilova AL, Bosnich B. *Chem Rev.* 2004; 104:349–384. [PubMed: 14871128]
3. (a) Velian A, Lin S, Miller AJM, Day MW, Agapie T. *J Am Chem Soc.* 2010; 132:6296–6297. [PubMed: 20397653] (b) Lin S, Day MW, Agapie T. *J Am Chem Soc.* 2011; 133:3828–3831. [PubMed: 21344904] (c) Lin S, Herbert DE, Velian A, Day MW, Agapie T. *J Am Chem Soc.* 2013; 135:15830–15840. [PubMed: 24066959] (d) Horak KT, Velian A, Day MW, Agapie T. *Chem Commun.* 2014; 50:4427–4429.
4. Dible BR, Sigman MS, Arif AM. *Inorg Chem.* 2005; 44:3774–3776. [PubMed: 15907100]
5. (a) Arduengo AJ, Harlow RL, Kline M. *J Am Chem Soc.* 1991; 113:361–363. (b) Herrmann WA, Köcher C. *Angew Chem Int Ed.* 1997; 36:2162–2187. (c) Díez-González S, Marion N, Nolan SP. *Chem Rev.* 2009; 109:3612–3676. [PubMed: 19588961] (d) Fortman GC, Nolan SP. *Chem Soc Rev.* 2011; 40:5151–5169. [PubMed: 21731956]
6. (a) Mata JA, Poyatos M, Peris E. *Coord Chem Rev.* 2007; 251:841–859. (b) Pugh D, Danopoulos AA. *Coord Chem Rev.* 2007; 251:610–641. (c) Poyatos M, Mata JA, Peris E. *Chem Rev.* 2009; 109:3677–3707. [PubMed: 19236010]
7. (a) Scheele UJ, John M, Dechert S, Meyer F. *Eur J Inorg Chem.* 2008; 2008:373–377. (b) Lee KM, Chen JCC, Lin IJB. *J Organomet Chem.* 2001; 617–618:364–375. (c) Scheele UJ, Dechert S, Meyer F. *Inorg Chim Acta.* 2006; 359:4891–4900. (d) Scheele UJ, Dechert S, Meyer F. *Tetrahedron Lett.* 2007; 48:8366–8370. (e) Li Y, Yang L, Chen Q, Cao C, Guan P, Pang G, Shi Y. *Z Anorg Allg Chem.* 2013; 639:575–581. (f) Liu B, Chen C, Zhang Y, Liu X, Chen W. *Organometallics.* 2013; 32:5451–5460. (g) Reindl SA, Poethig A, Drees M, Bechlers B, Herdtweck E, Herrmann WA, Kuehn FE. *Organometallics.* 2013; 32:4082–4091. (h) Yang L, Zhao J, Li Y, Ge K, Zhuang Y, Cao C, Shi Y. *Inorg Chem Commun.* 2012; 22:33–36. (i) Zhao J, Yang L, Ge K, Chen Q, Zhuang Y, Cao C, Shi Y. *Inorg Chem Commun.* 2012; 20:326–329. (j) Zhou Y, Xi Z, Chen W, Wang D. *Organometallics.* 2008; 27:5911–5920.
8. Andersen RA, Faegri K, Green JC, Haaland A, Lappert MF, Leung WP, Rypdal K. *Inorg Chem.* 1988; 27:1782–1786.
9. Lemonnier J-FoGuénée L, Bernardinelli GrVigier J-FoBocquet B, Piguet C. *Inorg Chem.* 2010; 49:1252–1265. [PubMed: 20050599]
10. Irrgang T, Keller S, Maisel H, Kretschmer W, Kempe R. *Eur J Inorg Chem.* 2007; 2007:4221–4228.
11. Burstein C, Lehmann CW, Glorius F. *Tetrahedron.* 2005; 61:6207–6217.
12. (a) Alcarazo M, Roseblade SJ, Cowley AR, Fernández R, Brown JM, Lassaletta JM. *J Am Chem Soc.* 2005; 127:3290–3291. [PubMed: 15755141] (b) Fürstner A, Alcarazo M, Krause H, Lehmann CW. *J Am Chem Soc.* 2007; 129:12676–12677. [PubMed: 17910460] (c) Alcarazo M, Stork T, Anoop A, Thiel W, Fürstner A. *Angew Chem Int Ed.* 2010; 49:2542–2546. (d) Ondrusek BA, Opalka SM, Hietsoi O, Shatruck M, McQuade DT. *Synlett.* 2013; 24:1211–1214.
13. (a) Mankad NP, Gray TG, Laitar DS, Sadighi JP. *Organometallics.* 2004; 23:1191–1193. (b) Kaur H, Zinn FK, Stevens ED, Nolan SP. *Organometallics.* 2004; 23:1157–1160.
14. (a) Danopoulos AA, Braunstein P, Stylianides N, Wesolek M. *Organometallics.* 2011; 30:6514–6517. (b) Danopoulos AA, Braunstein P. *Dalton Transactions.* 2013; 42:7276–7280. [PubMed: 23508380]
15. Lee CH, Laitar DS, Mueller P, Sadighi JP. *J Am Chem Soc.* 2007; 129:13802–13803. [PubMed: 17944470]
16. Suseno S, Horak KT, Day MW, Agapie T. *Organometallics.* 2013; 32:6883–6886. [PubMed: 24532865]
17. Jeoung JH, Dobbek H. *Science.* 2007; 318:1461–1464. [PubMed: 18048691]

18. Aresta M, Nobile CF, Albano VG, Forni E, Manassero M. J Chem Soc, Chem Commun. 1975:636–637.
19. (a) Bianchini C, Mealli C, Meli A, Sabat M. Inorg Chem. 1984; 23:2731–2732.(b) Anderson JS, Iluc VM, Hillhouse GL. Inorg Chem. 2010; 49:10203–10207. [PubMed: 20883021] (c) Gonzalez-Sebastian L, Flores-Alamo M, Garcia JJ. Dalton Transactions. 2011; 40:9116–9122. [PubMed: 21814687] (d) Beck R, Shoshani M, Krasinkiewicz J, Hatnean JA, Johnson SA. Dalton Transactions. 2013; 42:1461–1475. [PubMed: 23169546]
20. Fullmer BC, Fan H, Pink M, Caulton KG. Inorg Chem. 2008; 47:1865–1867. [PubMed: 18284191]
21. Horn B, Limberg C, Herwig C, Braun B. Chem Commun. 2013; 49:10923–10925.
22. (a) DeLaet DL, Del Rosario R, Fanwick PE, Kubiak CP. J Am Chem Soc. 1987; 109:754–758.(b) Ratliff KS, Lentz RE, Kubiak CP. Organometallics. 1992; 11:1986–1988.(c) Simon-Manso E, Kubiak CP. Organometallics. 2004; 24:96–102.
23. Jutzi P, Redeker T, Neumann B, Stammeler HG. J Organomet Chem. 1995; 498:127–137.
24. Horn B, Limberg C, Herwig C, Feist M, Mebs S. Chem Commun. 2012; 48:8243–8245.

**Figure 1.**

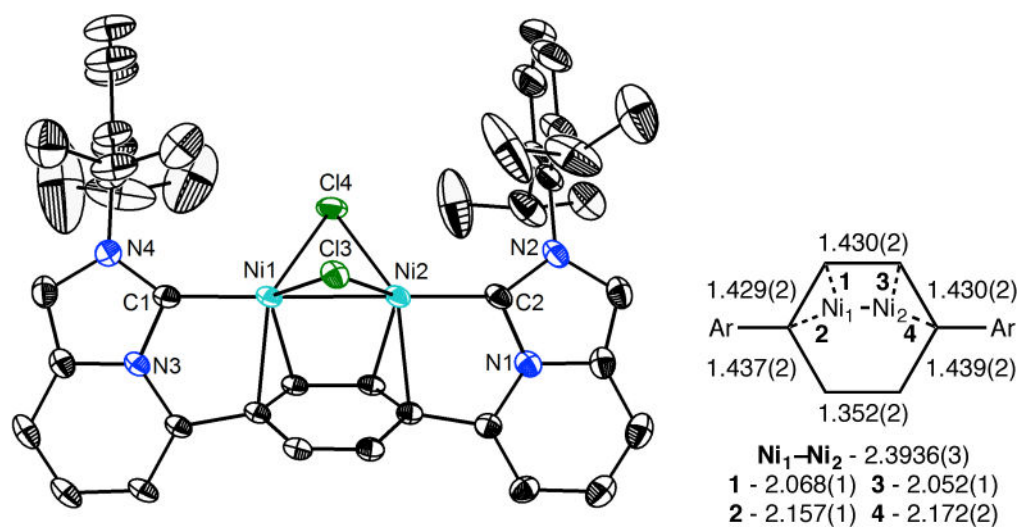
Dinickel(I) dichloride complexes supported by diphosphine **A** (**1**, left)<sup>3a</sup> and by N-heterocyclic carbene ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr, center).<sup>4</sup> This work: dinucleating bis(N-heterocyclic carbene) framework DIPr (right).



**Figure 2.**

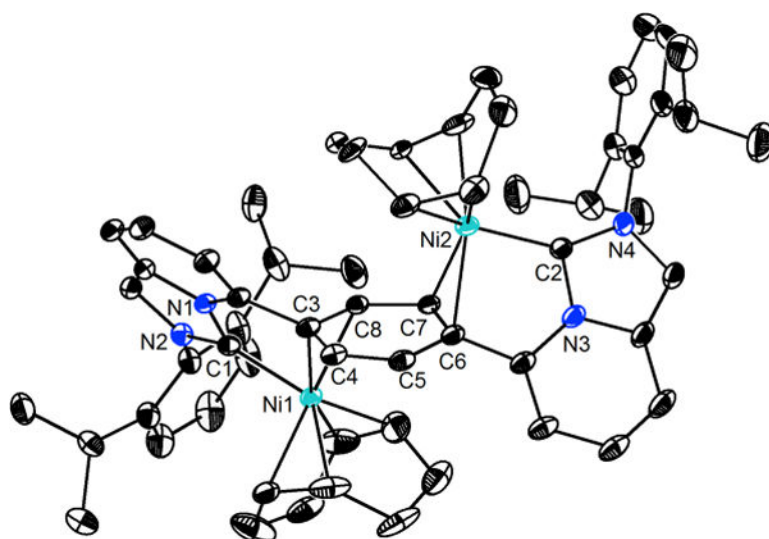
Solid-state structures of **2** (left) and **3** (right) as 50% thermal ellipsoids. Hydrogen atoms and solvent molecules not shown for clarity. Structure of **2** contains a mixture of bromide and chloride ligands.



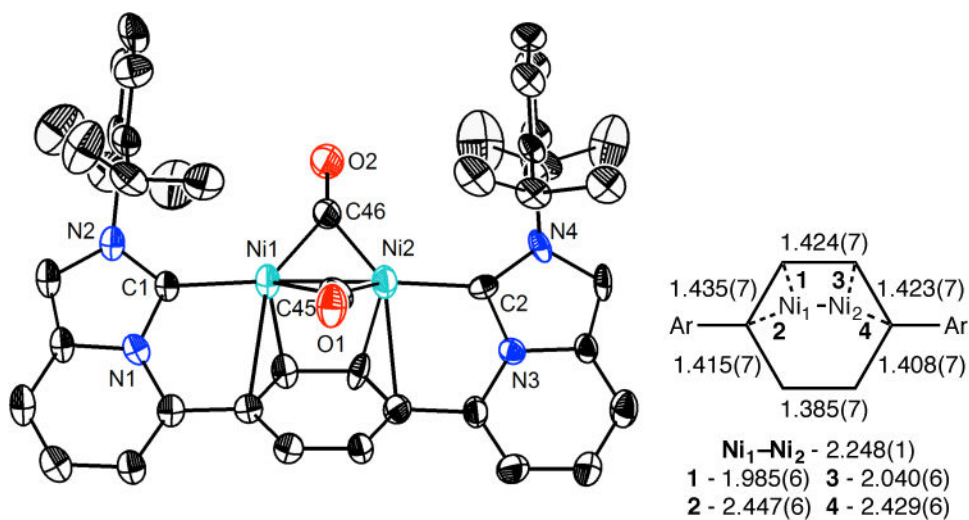


**Figure 3.**

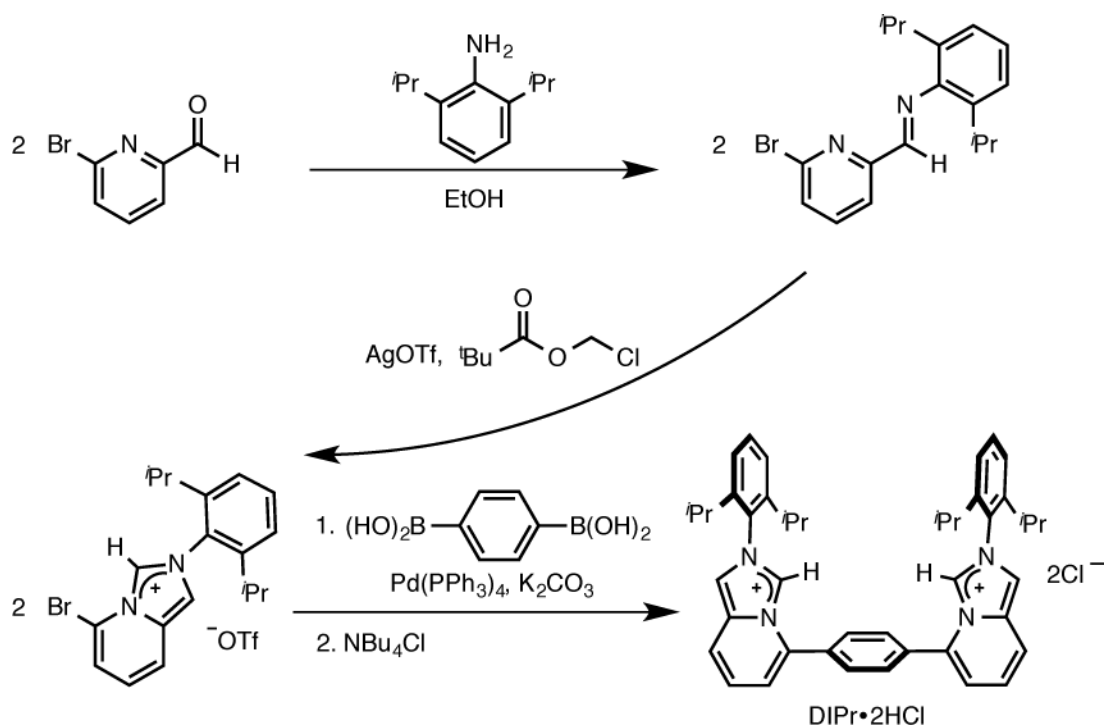
Solid-state structure of DIPr[Ni( $\mu$ -Cl)]<sub>2</sub> (**4**) as 50% thermal ellipsoids. Hydrogen atoms and solvent molecules not shown for clarity. Inset: selected bond distances (Å).



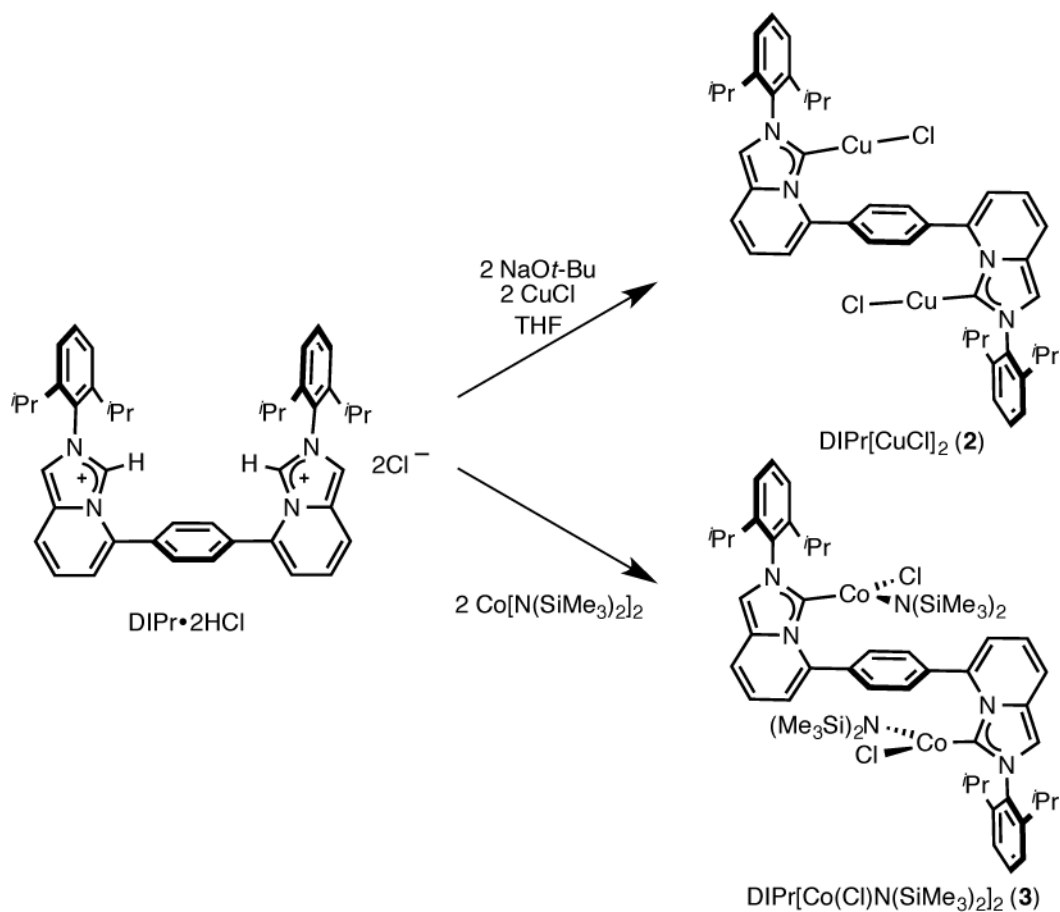
**Figure 4.** Solid-state structure of  $\text{DIPr}[\text{Ni}(\text{COD})_2]$  (**5**) as 50% thermal ellipsoids. Hydrogen atoms and outer sphere solvent molecules not shown for clarity.



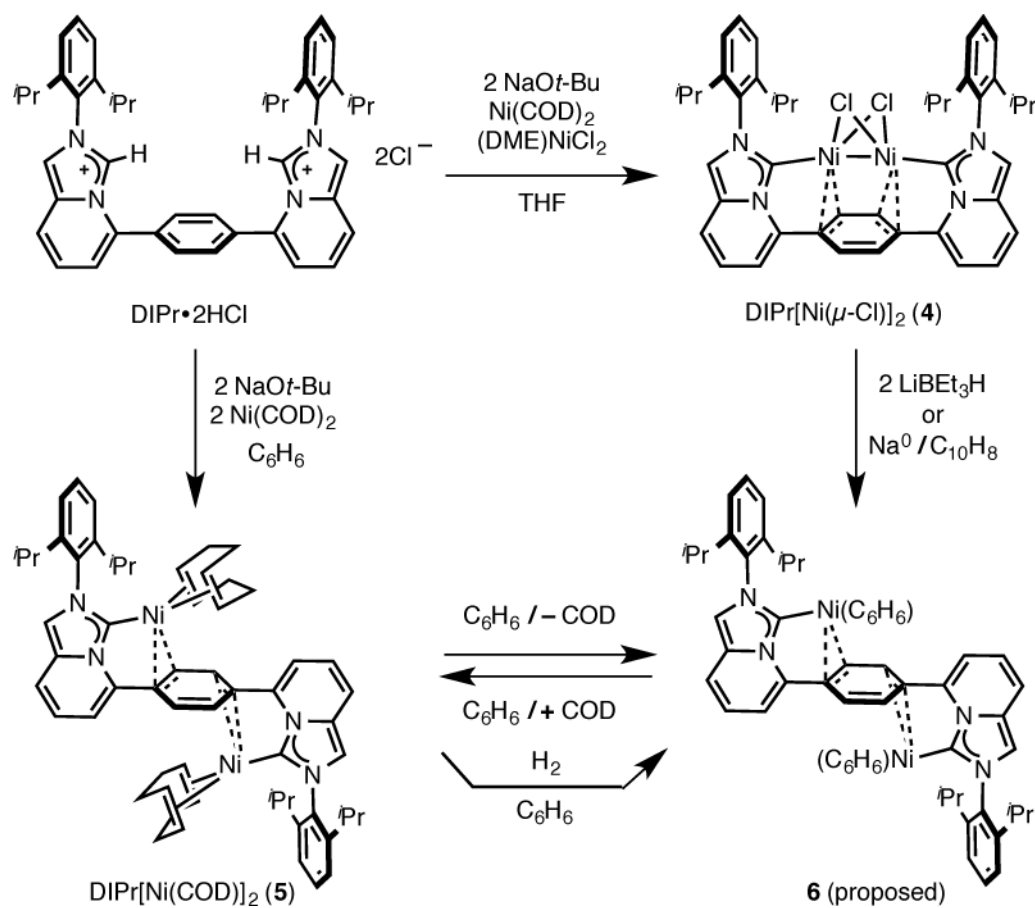
**Figure 5.** Solid-state structure of **7** as 50% thermal ellipsoids. Hydrogen atoms and solvent molecules not shown for clarity. Inset: selected bond distances (Å).



**Scheme 1.**  
Synthesis of DIPr•2HCl.

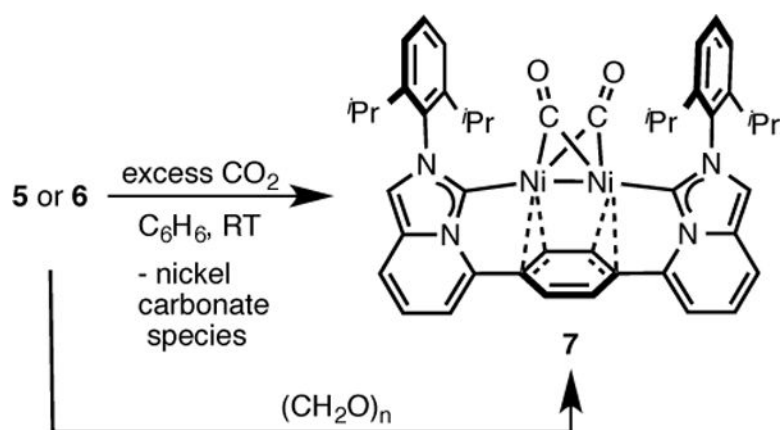
**Scheme 2.**

Synthesis of dicopper(I) compound **2** and dicobalt(II) compound **3**.



**Scheme 3.**  
Synthesis of dinickel complexes.



**Scheme 4.**Reaction of dinickel(0) complexes **5** and **6** with CO<sub>2</sub>.